Concentrations and source identification of organochlorine pesticides (OCPs) in soils from Wolong Natural Reserve

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In order to understand the distribution profile, composition characteristics and sources of OCPs, soil samples collected from Wolong Natural Reserve (WNR) in spring and autumn in 2005 were analyzed using gas chromatography coupled with electron capture detector (GC-ECD). Results showed that all OCPs concentrations were in the range of 10^{-2} ng/g—10^{-1} ng/g, representing the background level in those remote sites. Generally, their concentrations were slightly higher in spring than in autumn, which could be explained by OCPs: 1) may be released to soil from snow-melting water in spring; 2) partially evaporate into air from soil due to high temperature and intense radiation in summer and 3) can be relatively high degradation rate in summer. There were notable differences of OCPs seasonal variations between samples from alpine meadow and those from under-treeline. This phenomenon was related to physical-chemical properties of OCPs and vegetation coverage. For alpine meadow soils, levels of OCPs were increased with increasing altitudinal gradient, which was associated with enhanced scavenging efficiency of wet precipitation. Composition characteristics of OCPs in soils were similar to those of air samples, which was distinct from those of typical contaminated soils, indicating that OCPs in WNR soils were mainly from atmospheric transport.

Organochlorine pesticides (OCPs), such as hexachloro-cyclohexane (HCHs), dichloro-diphenyl-trichloroethane (DDTs) and hexachlorobenzene (HCB), are grouped into persistent organic pollutants (POPs) that have been banned for two or three decades in many countries including China. However, they are ubiquitous in the environment as a consequence of high lipophilicity, bioaccumulation, resistance to degradation, and propensity to undergo long-range transport, and even they can be found in high latitude or high altitude remote areas, like polar regions[1−3], Tibetan Plateau[4,5] and high mountains[6]. The transport mechanism, called the global distillation effect, describes the processes that semivolatile compounds emitted from diffusive sources at low-mid latitudes were transported to the higher latitudinal or altitudinal sites by atmospheric or aquatic transfer. Ecosystems in clean areas may be threatened by this mechanism; therefore, more attention should be paid to investigations on POPs levels, transfer and composition characteristics, especially in the high mountains.

Soils play an important role in the global distribution and fate of POPs because they not only have a large retention capacity but also re-emit these old organic pollutants into air as secondary source[7,8]. Researchers have observed that soils from remote areas were contaminated by POPs[1,4,6,9]. Soil loads of POPs reflect its flux from

air to soils[7], which depends on soil application as well as its physicochemical properties such as volatilization, degradation and leaching that are greatly affected by temperatures[10,11].

Wolong Natural Reserve (WNR) in mountain area of western Sichuan Province was studied as a representative location. Soil concentrations of HCHs, DDTs, and HCB were measured. The distribution profiles along the altitudinal transect, composition characteristics and atmospheric transport of OCPs as well as the influences of seasonal variations, site elevation and vegetations coverage were discussed.

1 Experimental

1.1 Study area

WNR, located in the west mountains of Sichuan Province and the east edge of the Tibetan Plateau (E102°52′－103°24', N30°45′－31°25'), is a national nature reserve and famous for an endangered species, giant panda. Gengda River and Pitiao River, the upper branches of Minjiang River, flow through the central area of WNR. The altitude of mountains to the southeast of Pitiao River is generally less than 4000 m, whereas that to the northwest of this river is almost about 5000 m.

WNR is governed by Tibetan Plateau's climate regime. In the winter half year (from November to the next April), WNR is mainly controlled by the southern branch of the westerlies, while in the summer half year (from May to October), this region is under the influence of southeast monsoon. WNR is an ideal area for investigating the distribution, transport and composition characteristics variation of POPs due to its unique features in geography, ecology and topography.

1.2 Sampling

Considering that OCPs concentrations may vary along with the change of climatic feature, soils were collected in the middle of April, 2005 (the end of winter half year) and the middle of October, 2005 (the end of summer half year), respectively (Table 1). According to the situation of vegetation cover and land application, soil samples collected along an altitudinal gradient were classified into two groups: one from alpine meadow (above Beimuping site) and the other from under-treeline (below Dengsheng site).

In each sampling site, surface soils (upper 10 cm) were sampled at 3 to 5 spots within a circular area with a diameter of 20 m and homogenized into a bulk one using a solvent-washed stainless steel scoop. The residual soils on the scoop were scraped by local soils before collecting the next sample. Soil samples were immediately wrapped in aluminum foils heated at 450 ℃ for 4 h in the laboratory, then packed into airtight polyethylene bags, delivered to the laboratory and kept frozen at −20℃ until analysis.

1.3 Reagent and materials

The extract solvents of *n*-hexane and dichloromethane were of pesticides residue grade (Tedia, USA). Florisil PR (100－200 mesh, Supelco Inc., USA) was activated in the oven at 170℃ for 13 h. Anhydrous sodium sulfate was of analytical grade and was baked at 450℃ for 4 h. The activated Florisil PR and anhydrous sodium sulfate were stored in a sealed desiccator.

Table 1 Descriptions of the sampling sites and organic carbon content in soil samples in 2005

Site No.	Name	Altitude (m.a.s.l.)/annual average temperature (℃)	Vegetation and land application	Sample No.	SOC(%)	
					Spring	Autumn
1	Tangfang	3940/−1.4	alpine meadow	S01	4.9	4.6
2	95 km site of 303 provincial highway	3619/1.4	alpine meadow	S02	9.3	12
3	Beimuping	3377/2.8	hardy scrub and alpine meadow	S03	10	11
				S04	10	10
4	Dengsheng	2828/6.1	fir	S05	6.5	7.1
5	Lvlvdian	2636/7.3	coniferous-broadleaved mixed forest and agriculture	S06	7.7	5.5
6	Sandao Bridge	2190/10.0	coniferous-broadleaved mixed forest	S07	3.0	2.8
7	Hetaoping	1847/12.1	Larch, coniferous-broadleaved mixed forest	S08	5.4	9.6
8	Gengda Town	1439/14.5	indeciduous/deciduous broadleaved mixed forest	S09	3.7	
9	Shuijiepai	1242/15.7	indeciduous/deciduous broadleaved mixed forest	S10	11	7.0

The OCPs standards of α-HCH, β-HCH, γ-HCH, δ-HCH, HCB, p,p'-DDE, p,p'-DDD, p,p'-DDT, o,p'-DDT and internal standard pentachloronitrobenzene (PCNB) were purchased from National Research Center for Certified Reference Materials of China. Two surrogate standards (2,4,5,6-tetrachloro-m-xylene, TMX and decachlorobiphenyl, PCB209) were purchased from J&K Inc.

1.4 Extraction and purification

Samples were freeze-dried and pulverized to sieve at 40 mesh until becoming homogenous. A 5-g sample with activated copper powder, spiked with surrogate standards (10 ng TMX and 40 ng PCB209), was extracted with 60 mL 1:1 (V/V) n-hexane and dichloromethane for 0.5 h using ultrasonic bath. The sample was stood overnight, then sonicated again for another 0.5 h and centrifuged. The extracts were reduced to 1—2 mL with rotary evaporator. The OCPs purification was conducted on a chromatography column (17 mm i.d), packed with 6 g florisil and 2 cm sodium sulfate from the bottom to top, which was conditioned with 50 mL 1:4 (V/V) n-hexane and dichloromethane. The elution was done with 70 mL 1:4 (V/V) dichloromethane and n-hexane. The eluates were concentrated to 200 μL under a gentle stream of pure nitrogen, and 8 ng PCNB was added as internal standard before GC analysis.

1.5 Instrumental analysis

The sample extracts were analyzed on an Agilent 6890 gas chromatography (GC) coupled with an electron capture detector (ECD). The separation was accomplished with an HP-5 fused silica capillary column (30 m×0.32 mm i.d.×0.25 μm film thickness). One μL sample extract was injected with splitless mode. The carrier gas was high purity nitrogen. The oven temperature program was as follows: 80℃ for 1 min, ramped at 10℃ min^{-1} to 180℃, held for 5 min, ramped at 2.0℃ min^{-1} to 200℃, ramped at 1.0℃ min^{-1} to 215℃, held for 4 min, and finally ramped at 25.0℃ min^{-1} to 280℃ and held for 5 min. The temperatures of injector and detector were 250℃ and 330℃, respectively. Identification of OCPs was determined by retention time. A five-point calibration was carried out using an internal standard method.

1.6 Quality control

All solvents used have no interfering peaks according to GC analysis. A procedure blank and a sample duplicate were processed for every 8 samples. In the blank procedure, HCB, α-HCH and γ-HCH had been shown to be 3 times higher than signal/noise of GC; thereby, all data were blank-corrected. The relative standard derivation (RSD) values of OCPs, with five duplicated measurements, were less than 20%. The recovery of surrogates was 76 ± 6.6% for TMX and 98 ± 7.1% for PCB209 respectively. A calibrated standard was measured to monitor GC performance after 10 injections. The degradation of p,p'-DDT in injector was <15% for daily check.

2 Results and discussion

2.1 Concentrations of OCPs

Table 2 shows the OCPs concentrations in soils at WNR and a comparison with other clean areas. It was shown that OCPs concentrations in WNR soils were generally low. In spring, the concentrations of ΣHCHs ranged

Table 2 Concentrations of OCPs found in the soils from WNR and comparison with other mountainous areas (ng/g)

	This work[a]		Soils from other clean areas		
	Spring	Autumn	Tibet[4]	Teide, Spain[12]	Antarctic area[1]
α-HCH	0.20(0.015—0.47)	0.084(0.063—0.53)	0.10—2.55	0.059±0.12	0.09—3.9
β-HCH	0.042(0.014—0.65)	0.041(0.025—0.14)	nd—1.29	–	0.03—0.32
γ-HCH	0.58(0.089—1.04)	0.24(0.11—0.33)	0.05—1.77	0.049±0.1	0.71—55
δ-HCH	0.034(0.009—0.11)	0.028(nd—0.033)	nd—0.03	0.0015±0.0029	0.00—0.57
ΣHCHs	0.64(0.15—1.35)	0.40 (0.23—0.80)	0.18—5.38	–	0.86—59.7
p,p'-DDE	0.17(0.058—1.04)	0.18(0.096—0.24)	0.00—2.83	3.4±7.9	0.03—3.19
p,p'-DDD	nd(nd—0.15)	0.007(nd—0.022)	nd—0.36	–	0.03—3.1
o,p'-DDT	0.11(nd—0.45)	0.088(0.055—0.15)	nd—0.34	–	0.00—6.27
p,p'-DDT	0.23(0.15—1.81)	0.19(nd—0.29)	nd—0.52	2.0±4.3	0.04—15
ΣDDTs	0.64 (0.34—3.15)	0.37 (0.21—0.66)	nd—2.83	5.4(0.01-40)*	0.1—25.6
HCB	0.083(0.02—0.20)	0.13(0.054—0.64)	–	0.31±0.55	0.02—25

a) The median value with range in parenthesis; nd: not detected; *: The mean of sum of p,p'-DDE and p,p'-DDT in ref. [12].

from 0.15 ng/g to 1.35 ng/g (median, 0.64 ng/g). These values were comparable to those reported in Tibet and lower than those in Antarctic, but slightly higher than those in Teide clean mountain area, Tenerife, Spain. ΣDDTs were between 0.34 ng/g and 3.15 ng/g (median, 0.64 ng/g), which were similar to those in soils from Tibet and mostly lower than the concentrations reported from Antarctic and Teide mountain area. HCB, 0.02－0.20 ng/g (median, 0.083 ng/g), was consistent with the concentrations detected in soils from Antarctic and Teide mountain area and close to the global background value of 0.68 ng/g[13]. OCPs concentrations in autumn soil were lower than those in spring soil. The results indicated that WNR is a pristine region.

2.2 Seasonal variations of OCPs

Soil organic matter (SOC) is generally regarded as a preferential medium for the sorption of hydrophobic pollutants. In order to elucidate the adsorption of OCPs by soil, the contents of SOC were measured (Table 1). Then the OCPs concentrations were normalized to SOC (Tables 3 and 4).

HCHs: Concentrations of HCHs were low in most spring soils, indicating that WNR is a pristine area. However, an exceptional high concentration was found at Sandaoqiao site (S07), possibly resulting from the local contamination. The altitudinal variations of HCHs in autumn were in agreement with those in spring. The concentration of HCHs in S07 was again the highest in autumn, which further confirmed the existence of local

contamination. The percentages of β-HCH to ΣHCHs in S07 were 55% in spring and 36% in autumn, respectively, much higher than the other sites. High level of HCHs in S07 was caused by relatively abnormal value of β-HCH.

DDTs: DDTs concentrations, especially p,p′-DDT in spring soils from under-treeline sites, were higher than those from alpine meadow sites (Table 3). In contrast with the other three chemicals, the concentrations of p,p′-DDT were much higher. While in autumn soils, concentration variations of DDTs along the altitudinal gradient were not significant. The percentage of p,p′-DDE approached to p,p′-DDT which was still predominant among DDTs (Table 4).

HCB: Concentrations of HCB in spring and autumn soils were similar (Tables 3 and 4). It is known that HCB is extremely persistent in the environment. Among OCPs mentioned above, HCB is the most volatile with strong persistence, low water solubility and a long half-life (about 80 days or even much longer) in air. Therefore, it is prone to disperse thoroughly and undergo long-range atmospheric transport[13]. The atmospheric transport is an efficient way for the POPs to redistribute from contaminated lands to pristine soils, resulting in homogenous contents of POPs on a large scale in remote area. In this study, concentrations of HCB based on dry weight in WNR soils were at the level of global background value, so it could be inferred that HCB in WNR soils was mainly from atmospheric transport.

Table 3 Soil organic carbon-normalized concentrations of OCPs in soils from WNR, in spring in 2005 (ng/g (SOC))

Sample	HCHs					DDTs					HCB
	α-HCH	β-HCH	γ-HCH	δ-HCH	ΣHCHs	p,p′-DDE	p,p′-DDD	o,p′-DDT	p,p′-DDT	ΣDDTs	
S01	3.6	1.2	21	1.6	28	3.1	ND	1.4	3.4	7.9	3.7
S02	1.6	0.35	4.6	0.36	6.9	1.7	ND	1.2	2.3	5.2	1.9
S03	2.3	0.22	1.5	0.095	4.1	1.2	ND	0.46	1.9	3.6	0.71
S04	2.7	0.24	2.9	0.13	6.0	1.0	ND	0.77	1.5	3.3	1.1
avg.	**2.5**	**0.49**	**7.6**	**0.55**	**11**	**1.8**		**0.96**	**2.3**	**5.0**	**1.9**
RSD%	**32**	**92**	**122**	**131**	**99**	**53**		**44**	**37**	**43**	**71**
S05	1.4	0.65	5.0	0.31	7.3	4.1	ND	2.3	3.5	9.9	3.1
S06	3.9	0.18	1.3	0.23	5.6	0.75	ND	0.54	ND	1.3	0.52
S07	6.5	21	7.1	3.8	39	5.6	ND	ND	5.8	11	0.59
S08	7.8	1.9	8.1	0.66	18	3.9	0.33	3.9	6.2	14	1.5
S08[a)]	8.7	1.8	8.9	0.85	20	3.8	0.36	4.1	6.9	15	1.5
S09	0.40	0.94	2.4	0.24	4.0	5.4	0.49	6.2	7.5	20	1.1
S10	1.6	3.0	2.7	0.41	7.6	9.2	1.3	4.0	13	28	1.5
avg.	**4.3**	**4.3**	**5.1**	**0.92**	**15**	**4.7**	**0.63**	**3.5**	**7.2**	**14**	**1.4**
RSD%	**78**	**179**	**60**	**138**	**85**	**55**	**77**	**54**	**46**	**58**	**61**

a) the duplicate of S08.

Comparison of seasonal variations: The percentage of the mean concentration difference (PMCD) of OCPs in soils between spring and autumn is presented in Table 5. The results showed that for alpine meadow soils, PMCD of HCHs was higher than that of DDTs (ΣHCHs ＞ΣDDTs), and PMCD of HCB was similar to that of ΣDDTs. For under-treeline soils, PMCDs of ΣHCHs and ΣDDTs were similar to each other while HCB was close to zero. Compared with the physicochemical properties of these three kinds of OCPs, the LogK_{AW} of HCHs is lower than DDTs and much lower than HCB, indicating that HCHs could be deposited more readily into terrestrial surface through wet precipitation. Similarly, Log-K_{OW} of HCHs is also smaller compared with those of DDTs and HCB, which means that HCHs are less retainable by organic-matter-rich compartments. Moreover, water solubility of HCHs is larger than the other two kinds of OCPs. Therefore, when these three kinds of

OCPs release into terrestrial compartments, HCHs are most unlikely to be retained and therefore, behave more actively relative to DDTs and HCB.

The dominant precipitation in WNR is often in the form of snow in winter half year and in the form of rain in summer half year. In winter cold season, organic contaminants in air can be effectively scavenged by snow. Specially, HCHs could be scavenged more efficiently than DDTs and HCB due to their physicochemical properties. Compared with rain, snow has a longer time to remain on the surface of land, thereby providing more opportunities for organic chemicals scavenged to be delivered into land surface with the snowmelt water. Therefore, the process of snowmelt in spring has a larger contribution for transferring HCHs to soil than that of DDTs and HCB. By contrast, in summer, the organic chemicals scavenged by abundant rain had less time to interact with soils because residence time of rain on the

Table 4 Soil organic carbon-normalized concentrations of OCPs in soils from WNR, in autumn in 2005 (ng/g (SOC))

Sample	HCHs					DDTs					HCB
	α-HCH	β-HCH	γ-HCH	δ-HCH	ΣHCHs	p,p'-DDE	p,p'-DDD	o,p'-DDT	p,p'-DDT	ΣDDTs	
S01	1.4	1.2	5.3	0.63	8.4	2.1	0.24	1.2	1.1	4.6	1.9
S02	1.7	0.35	1.2	0.28	3.5	1.8	0.10	1.3	2.5	5.7	2.2
S03	1.5	0.23	0.95	0.13	2.8	1.5	0.06	0.97	2.6	5.2	1.5
S04	5.2	0.25	2.5	ND	7.9	1.8	ND	0.95	2.5	5.2	2.1
avg.	**2.4**	**0.50**	**2.5**	**0.35**	**5.7**	**1.8**	**0.13**	**1.1**	**2.2**	**5.2**	**1.9**
RSD%	**76**	**91**	**79**	**75**	**51**	**13**	**72**	**15**	**34**	**8.4**	**16**
S05	1.1	0.38	1.5	0.20	3.2	2.4	ND	0.83	1.4	4.6	9.0
S06	1.6	0.69	6.0	0.54	8.8	2.4	0.39	1.5	3.4	7.6	1.1
S07	2.3	5.1	5.9	1.0	14	7.3	0.78	2.4	5.6	16	1.9
S08	0.88	0.49	2.5	0.17	4.1	1.9	ND	1.1	1.5	4.5	0.73
S10	1.2	0.65	4.5	0.23	6.5	3.5	ND	1.3	ND	4.7	1.9
avg.	**1.4**	**1.5**	**4.1**	**0.43**	**7.4**	**3.5**	**0.58**	**1.4**	**3.0**	**7.5**	**2.9**
RSD%	**39**	**139**	**49**	**83**	**60**	**64**	**46**	**42**	**67**	**66**	**116**

ND: not detected.

Table 5 Difference of average concentration (normalized with SOC content) between spring and autumn for alpine meadow and under-treeline soils, respectively*

	logK_{AW}	C_L(mol/m³)	logK_{OW}	logK_{OA}	Soils from alpine meadow Δ%	Soils from under-treeline Δ%
α-HCH	−3.53	0.333	3.94	7.46	4.6	70
β-HCH	−4.83	1.44	3.91	8.74	−2.4	61
γ-HCH	−3.91	0.247	3.83	7.74	67	23
δ-HCH					37	37
ΣHCHs					49	46
p,p'-DDE	−2.77	0.00079	4.2	9.70	−1.3	26
p,p'-DDD	−3.7	0.0023	6.33	10.03		7.5
o,p'-DDT					−15	60
p,p'-DDT	−3.34	0.00042	6.39	9.73	5.0	59
ΣDDTs					−3.1	47
HCB	−1.57	0.0014	5.64	7.21	−3.4	−0.9

*: D%＝(spring mean concentration-autumn mean concentration)/spring's*100. Calculation of HCHs did not include S07 value for contaminated site. In calculation of HCB, S05 was excluded. Physical-chemical properties were adjusted at 25℃[14,15].

land surface was relatively short. Furthermore, because of the higher water solubility, HCHs were easier to dissolve and be washed out with surface runoff than the others. All these factors described above may lead to the most significant seasonal variation of HCHs concentration in soil. Meanwhile, alpine meadow area is far away from anthropogenic activities and has sparse vegetation cover and low capacity of soil to retain the chemicals. Higher HCHs PMCD in this area could be attributed to these factors.

Under-treeline samplings were close to human living area. The sampling sites were characterized by dense vegetation cover and organic-rich soil, which favored uptake of organic chemicals. Because LogK_{OA} and log-K_{OW} of DDTs are higher than those of HCHs, DDTs could be more readily adsorbed by the lipid-rich media like vegetation. Table 1 shows that the under-treeline vegetation was mostly composed of indeciduous and deciduous broadleaved mixed forest. During leaf development in spring, the coverage of vegetation extends significantly. The filter and uptake effects of vegetation reduce the organic chemical concentration in air and aquatic system. DDTs with higher lipophilic were prone to be adsorbed by the plant cuticle[16] compared with HCHs and HCB. When sampling in autumn (October), the plants did not defoliate, and foliar uptake of DDTs did less transport from the canopy to soils. However, these DDTs could enter into surface media with a litter fall in late autumn, through long decay over winter, and finally enhanced the spring soil concentration. Therefore, PMCD (47%) of DDTs was clearly observed for under-treeline sites, while PMCD of DDTs was rather small (−3.1%) for alpine meadow sites. The vegetation filter and uptake effects on lower lipophilic HCHs were relatively weak[16] and consequently, the PMCD was similar for both alpine meadow and under-treeline sites. Additionally, the vegetation filter and uptake effects retained more organic chemicals in the terrestrial environment especially in forest soils[16]. Vegetation and cloud cover also reduced direct solar radiation, thus resulting in a relatively small rate of photolytic degradation, which may lead to the fact that mostly OCPs concentrations were slightly higher in under-treeline soils than alpine meadow soils. HCB was distributed evenly[13] and showed small seasonal variations due to the relatively strong volatilization (logK_{AW} = −1.57), which brought about small PMCD approaching to zero.

It was intriguing that seasonal concentration variations of most OCPs, higher in spring than autumn, were consistent with the result obtained by simulating the influence of snow on the fate of α-HCH[17]. WNR has high altitude and long wintertime with frequently dry and wet precipitation like snow and/or haze. The deposition of α-HCH was continuously accumulated in snowpack from November to the following April when snow cover existed. While the deposited α-HCH will be partially released to terrestrial compartments with snowmelt (including melt water and the particle flush), which leads to rising concentration in soil in spring. At high temperature and under intense microbes activity during summer, the re-evaporation and microbial degradation of α-HCH were enhanced, as well as plentiful rainfall impelling the loss of α-HCH, which resulted in slightly low soil concentration in autumn. The causes of other OCPs seasonal variations were similar to α-HCH.

2.3 Mountain cold condensation of OCPs

For alpine meadow soils, the concentrations of ΣHCHs, ΣDDTs and HCB increased with increasing altitudinal gradient along the mountain slope, showing "cold condensation". Previous research[18] pointed out that there are two preconditions for "cold condensation": the first is that all samples should be collected along the same mountain slope so that the sampling sites bear similar "emission sources-receptor" relationship. The other is free of local pollution sources. The alpine meadow sites in WNR satisfy these two preconditions.

The distribution profiles of OCPs in air were fairly uniform along the WNR altitudinal gradient. Due to the ascending height, decreasing temperature and the change of precipitation form, semivolatile organic compounds could partition into condensed phase (such as rain, snow and aerosol) with enhanced efficiency of precipitation scavenging[19]. Thus the enhanced deposition of OCPs to soil, vegetation and water would occur at the higher elevation, which led to the increasing trends of OCP levels. In this work, OCPs in alpine meadow soils displayed "cold condensation effect" (Table 3). However, the number of soil samples was limited in this work. Further studies are needed[20,21].

2.4 Source identification of OCPs

In order to identify the possible sources of OCPs in WNR, isomer ratios of HCHs and ratio of member
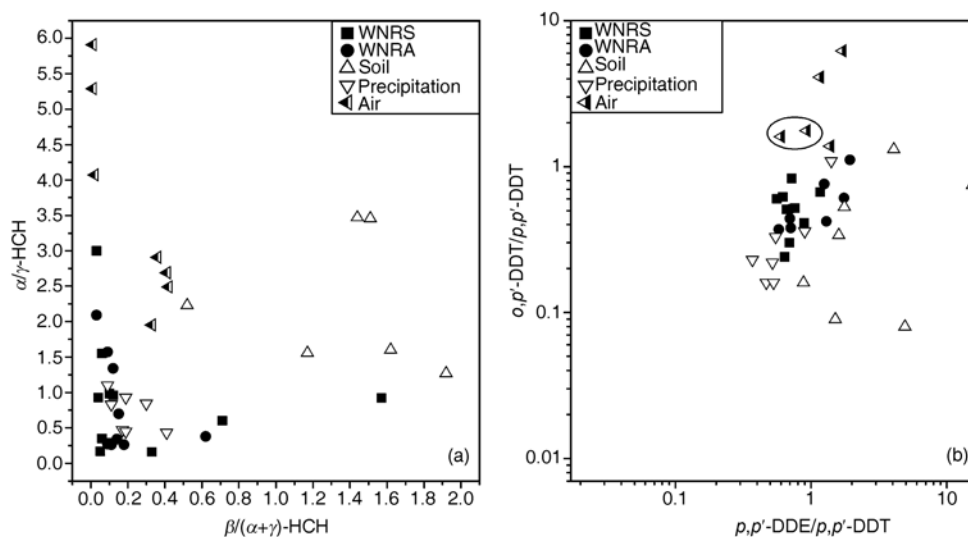
Figure 1 Comparison of the isomer ratios of OCPs in WNR soils with those in previous studies. WNRS: Spring soils at WNR; WNRA: Autumn soils at WNR. For convenient comparison, abscissa and ordinate of (b) refers to log-transformed axis.

compounds of DDTs in WNR soils were compared with those of contaminated soils[4,22−26] and air-related samples[27−33] (e.g., precipitation and air samples) in previous studies (Figure 1).

For HCHs, α-/γ-HCH was used as ordinate while β-/(α+γ)-HCH as the abscissa (Figure 1(a)). The α-/γ-HCH ratio in the technical HCH is around 3.6−15, while α-/γ-HCH ratio in lindane is less than 0.1. Therefore, α-/γ-HCH ratio was often used to distinguish the potential sources and long-range atmospheric transport of HCHs. The vapor pressures of α-HCH and γ-HCH are larger than β-HCH (Table 5), indicating that the former more easily exists in gas phase, while β-HCH is most stable and persistent among all HCH isomers due to symmetric chemical structure. Therefore, β-HCH will be the predominant isomers in soils with time elapse, and the proportion of β-HCH to the total HCHs is comparatively high in contaminated soil[34], suggesting that β-/(α+γ)-HCH can be used to differentiate whether HCHs are from aged contamination or not. By comparing the two kinds of ratios of this study with data from literature, the major sources of HCHs in WNR soils may be identified.

As shown in Figure 1(a), most ratios of HCHs in WNR soils were similar to air-related samples with β-/(α+γ)-HCH less than 0.5. And thus it could be inferred that HCHs in WNR soils were from atmospheric deposition. The β-/(α+γ)-HCH ratios of S07 and S10 were lager than 0.5, reflecting the characteristics of con-

taminated soils. S07 may be locally contaminated. Although low concentrations of HCHs were found in S10, the possibility of historical usage of this chemical can not be excluded in view of the relative low altitude and dense human activities at the site.

In general, p,p'-DDT will be degraded to p,p'-DDE under aerobic conditions whereas p,p'-DDD under anaerobic conditions. p,p'-DDE in the environment is mostly from the metabolite of p,p'-DDT. Therefore, the ratio of p,p'-DDE/p,p'-DDT could be used as a proxy to reveal the history period of DDTs released to the environment. Namely, low ratio of p,p'-DDE/p,p'-DDT indicates the recent usage of DDTs, and the ratio of o,p'DDT/p,p'-DDT could show whether there was usage of dicofol. Technical DDT includes less than 15% of o,p'-DDT and higher than 85% of p,p'-DDT, and the ratio of o,p'-DDT/p,p'-DDT was about 0.175. Although technical DDT was banned for agricultural purpose in China from 1983, dicofol as nonsystemic acaricide is still extensively used for the control of mites. In the technical dicofol, there are considerable impurities of DDTs in which the o,p'-DDT is the predominant species and the ratio of o,p'-DDT/p,p'-DDT is about 7[35].

Figure 1(b) shows that DDTs-related ratios in WNR soils in spring and autumn was also similar to air-related samples (including two air samples from WNR that are signed with a ellipse in Figure 1(b)), but was significantly different from the typical contaminated soils, implying that DDTs in WNR soils were from atmospheric deposition. p,p'-DDE/p,p'-DDT ratios in WNR soils ap-

proached to 1 (Figure 1(b)), suggesting the possible occurrence of fresh input of DDT in this area. The ratio of o,p'-DDT/p,p'-DDT was obviously larger than 0.175. As their half-life time for phytodegradation is similar[31], the high ratio of o,p'-DDT/p,p'-DDT in WNR air (larger than 1 (Figure 1), indicates fresh input of dicofol. Similar observations were reported for central-Himalayas spruce needles[5].

3 Summary

The concentrations of OCPs in WNR soils are relative low, which are comparable to those in typical pristine region such as Arctic, Antarctic and Tibetan Plateau. The low concentration of WNR implies this area is a suitable area to study long range atmospheric transport of POPs. Especially, alpine meadow sites were found to have no local contamination, fulfilling the preconditions of random sampling.

The environmental processes influencing the concentrations, distribution and seasonal variations of OCPs mainly include precipitation (particularly, snow scavenging in winter), snowmelt flush in spring, enhanced evaporation by high temperature and intense radiation in summer, vegetation filter and uptake of organic compounds during leaf development and microbial degradation.

Both composition characteristics of OCPs and "cold condensation" in alpine area demonstrated that OCPs in WNR soil were mainly from atmospheric transport. Soil, as major reservoir and secondary source, may play an important role in the global cycles of OCPs.

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